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Remarks on the lattice dynamics of alkali halide crystals

By Stig O. Lundqvist

With 2 figures in the text

ABSTRACT

In a couple of earlier papers [1, 2] a treatment of the lattice vibrations of the alkali halides has been proposed, starting from the Heitler–London approach and supplemented with terms accounting for the dipolar polarisation of ions in the lattice. A preliminary calculation along such lines has been reported in [3]. Recently a formally different scheme, the so-called shell model of lattice vibrations, based on a paper by Dick and Overhauser [4], has been successfully developed and applied by Cochran [5, 6, 7]. The purpose of this note is to reconsider the physical assumptions in [1] and [2] and show that the scheme proposed there is actually not restricted to the Heitler–London approximation and also to make clear that the physical content of our scheme and the shell model, although formally quite different, is essentially the same.

Introduction

The development of a theory of simple ionic crystals like the alkali halides has progressed along essentially two different lines: calculations from first principles and the construction of models directly from physical considerations. The *ab initio* type of investigations has up to now not essentially surpassed the approximation considered by Löwdin [8] in extensive calculations for several alkali halides. His work is based on the use of an antisymmetrized product of one-electron wave function for free ions. To be very explicit: the one-electron wave functions are rigidly connected to each ion and are not deformable (polarisable). This does not imply, however, that the crystal can be considered simply as a superposition of free ions in the lattice. On the contrary, the antisymmetry requirement imposes characteristic deviations from that charge distribution which would correspond to a simple superposition of ions. This modification of the charge distribution leads to certain effects which are in qualitative agreement with empirical facts. The additional term in the charge distribution gives rise to a three-body potential (in lowest order) in the expression for the lattice energy which in turn causes deviations from the Cauchy relation of the correct sign and order of magnitude [8]. Furthermore, in the high frequency limit of the vibration spectrum the same term leads to the introduction of an effective charge [1], which was originally introduced by Szigeti [9] from phenomenological considerations. As in the case of the elastic constants, the agreement is only qualitative.

To summarise those positive results of the Heitler–London theory which have some bearing on the problem of lattice oscillations: in most applications the binding energy and lattice constant have been given with fair accuracy and the theory accounts qualitatively for the deviations from the Cauchy relations and leads in a natural way to the introduction of an effective charge in the long-wave optical oscillations. On the negative side, the numerical results for the elastic constants and the effective charge are definitely not accurate enough to make the theory directly useful for studies of the vibration spectrum. Still more important, the effect of the electronic polarisation is now known to be of essential importance but is completely neglected in the theoretical scheme.

As no more satisfactory treatment of ionic crystals has yet been presented, a study of lattice oscillations from first principles is not possible at present. A possible approach to the problem, which seems to be somewhat less heuristic than a pure model approach, would be to consider those terms in the general expression for the lattice energy which seem to be most important in describing, e.g. the elastic and dielectric properties, and then reduce the expression to an approximate form such that all important parameters of the theory can be directly related to experimentally known quantities, thus avoiding the main inaccuracy of the quantum mechanical calculations. This was the attitude taken in [1] and [2] and it will be elaborated along somewhat different lines in this note.

Long before quantum mechanics, Born proposed a definite model for the interactions in an ionic solid, assuming a Coulomb interaction between point charge ions and in addition a strong repulsive central interaction of short range between ion pairs. This model has been extensively used in calculations of vibrational properties of alkali halides—the first successful applications were made independently by Kellermann [10] and Iona [11]. The apparent success of these applications must, however, be considered as rather fortuitous, as the Born model is inherently inadequate to describe important properties which are essential for the lattice dynamics of such crystals. The elastic properties are not correctly described because any model with central interactions only leads automatically to the Cauchy relation for a static lattice. Still more important is the failure to describe properly the long-wave optical oscillations of the lattice. These oscillations are now well understood on the basis of macroscopic theory (see, e.g. ref. [12]), and it has been shown that the Born model gives a poor description of these oscillations.

Recently a microscopic model for describing the dielectric properties has been proposed by Dick and Overhauser [4], which describes the physical situation in a simple pictorial way and has proved very useful. They consider an ion in the lattice as consisting of two parts: an inner core, which moves rigidly with the nucleus, and an outer spherical shell. This shell can move rigidly relative to the core and its motion is characterized by the displacement vector relative to the centre of the core and a spring constant attaching the shell to the core. This evidently accounts for the ordinary dipolar poarisation of the ions. An additional effect intimately related to the effective charge and due to short-range (exchange) deformations is accounted for by introducing a spring constant between neighbouring shells. This model has recently been developed by Cochran [5, 6, 7] into a scheme for studying lattice oscillations and has been very successfully applied to NaI and also to Ge.

In the following it will be discussed how the scheme developed in [1] and [2] can be justified as a semi-phenomenological approach on somewhat more general grounds than is clear from the discussion in those papers, and it should also be clear from this discussion that the physical content of that scheme is essentially the same as that of the shell model, although the formal descriptions are widely different.

Remarks on the long range interactions

A procedure, which has been extensively used for, e.g. covalent crystals, has been to assume that the interactions between the atoms have such a short range that they act only between the nearest neighbours or perhaps the next nearest neighbours. Even though the binding properties of such crystals can be well understood on this assumption, it will not hold for a distorted lattice, because the charge distribution around each atom will be deformed in such a way that the charge cloud around each atom will carry multipole moments of various orders, which will interact over appreciable distances. This was first developed quantitatively by Lax [13], who considered the quadrupole-quadrupole interactions in Ge and found good agreement with the dispersion curves obtained from neutron diffraction experiments—an agreement which cannot be obtained by assuming short-range interactions only.

In ionic crystals like the alkali halides one has, of course, from the very beginning to consider long-range interactions, as the main part of the cohesive energy is due to the Coulomb interaction between charged ions. In addition to the Coulomb interaction and the repulsive short-range interactions, one has also to consider the effects of the electric moments which will be associated with each ion in a distorted lattice. These electric moments result from a deformation of the charge distribution around each separate ion, and this deformation in turn is a consequence of destroying the high symmetry of the unperturbed lattice. In part the deformation is due to the strong local field present in a distorted lattice (ordinary polarisation), in part due to the exclusion principle (short-range deformation).

In general the importance of the various contributions should be as follows: in the first place the Coulomb and repulsive interactions, secondly the interaction between the charges and the multipoles, because the charges are zero-order terms, being present on the undisturbed lattice, and thirdly the interaction between the multipoles themselves. Obviously this division cannot be pursued too far, but it will provide a convenient starting point for our considerations, where we shall mainly be concerned with the charge–multipole interactions. It may at first seem rather arbitrary to consider multipoles associated with the separate ions, because the ions do not exist as well-defined entities inside a crystal. However, one can always make reference to a predetermined way of dividing the lattice into cells around each ion, and with respect to such a subdivision all moments will have a well-defined meaning.

The long-range interactions are evidently important for understanding the dielectric properties of the crystal. It should be remarked that they are equally important for the elastic properties. From the formula for the elastic constants (see e.g. (10), ref. [1]) it is obvious that even rather weak forces of long range can give appreciable contributions to the elastic constants because of the slow convergence of the lattice sums. As almost all empirical parameters which enter into calculations of vibration spectra refer to the long wave-length limit of acoustical and optical vibrations (elastic and dielectric constants), it seems essential to treat as properly as possible the most important long-range interactions.

We shall in the following mainly discuss those terms in the expression for the lattice energy which can be reduced to Coulomb and charge–multipole interactions. About the repulsive short-range interactions we shall explicitly assume that these can be represented by central two-body interactions. According to the general quantum mechanical expression for the lattice energy, this cannot be strictly true.

However, we shall not be concerned with crystals where, e.g. strong oriented bonds are present, which resist shearing forces in a complicated way, and there seem to be no indications at present that complicated non-central forces of short range will be of importance for the alkali halides.

The lattice potential

Instead of starting from the most general form of the lattice energy and successively reducing it to the appropriate form, we can in fact start directly from the approximate expression in the Heitler–London scheme and discuss the modification on the basis of this formula. The reason for this is that the charge–multipole interactions can be discussed in terms of the number density alone and for such interactions the modifications of the formulae are easily introduced. In a slightly different notation from that used in [1] and [2] the expression reads

$$\Phi=\frac{e^2}{2}\sum_G\sum_{G'}{}^{(G)}\frac{\varepsilon_G\varepsilon_{G'}}{|\mathbf{r}_G-\mathbf{r}_{G'}|}+e^2\sum_G\sum_{G'}v\left(|\mathbf{r}_G-\mathbf{r}_{G'}|\right)+$$

$$+e^2\sum_\mu\sum_\nu\sum_G{}^{(G_\mu\,G_\nu)}d_{\mu\nu}\left(\nu\left|\frac{\varepsilon_G}{|\mathbf{r}-\mathbf{r}_G|}\right|\mu\right). \tag{1}$$

Here e denotes the electron charge, ε_G denotes the valence of an ion at the lattice position G and $\mathbf{r}_G$ the position vector of that point. $v\left(|\mathbf{r}_G-\mathbf{r}_{G'}|\right)$ is a short hand notation for all the integrals which only depend on the relative distance between two nuclei and gives the repulsive potential. μ stands for all the quantum numbers nlms of an electron associated with an ion at a certain lattice point G. $(\mu|\varepsilon_G/|\mathbf{r}-\mathbf{r}_G|\mu)$ is the matrix element between two one-electron wave functions ψ_μ and ψ_ν associated with the same or different ions G_μ and G_ν and $\sum_G (G_\mu G_\nu)$ denotes a summation over lattice positions where G is always different from G_μ and G_ν.

When μ and γ are associated with different ions G_μ and G_ν then the $d_{\mu\nu}$ are identical with the overlap integrals and depend only on the distance $|\mathbf{r}_{G_\mu}-\mathbf{r}_{G_\nu}|$

$$d_{\mu\nu}=d_{\mu\nu}\left(|\mathbf{r}_{G_\mu}-\mathbf{r}_{G_\nu}|\right). \tag{2}$$

For $\mu=\nu$, $d_{\mu\mu}$ is a sum of independent contributions from the ions surrounding i, thus

$$d_{\mu\mu}=\sum_G{}^{(G_\mu)}e_{\mu\mu}\left(|\mathbf{r}_{G_\mu}-\mathbf{r}_G|\right). \tag{3}$$

The first term represents the Coulomb interaction between point-charge ions. The reduction of the general quantum mechanical expression can be made such that this term remains as in (1). The next term is the repulsive interaction and will by assumption have such a form. The last term in (1) corresponds formally to a three-body interaction and has a simple physical interpretation. The number density $n(\mathbf{r})$ of eclectrons has the form

$$n(\mathbf{r})=\sum_G n_G(\mathbf{r})+\Delta n(\mathbf{r}) \tag{4}$$

with

$$\Delta n(\mathbf{r})=\sum_\mu\sum_\nu d_{\mu\nu}\psi_\mu(\mathbf{r}). \tag{4'}$$

$n_\mu(\mathbf{r})$ gives the electron distribution in a free ion at the position G. $\Delta n(\mathbf{r})$ represents the deviations from the distribution which would correspond to a simple superposition of free ions and is in the Heitler–London picture only a consequence of the antisymmetry requirement on the wave function.

Comparison between (4) and the last term in (1) shows that the three-body term in (1) represents the electrostatic interaction between the charge distribution $\Delta n(\mathbf{r})$ and a point charge lattice. Following the arguments in [1] it can easily be expanded in a multipole series and the last term has therefore an obvious interpretation as a sum of charge–multipole interactions. These interactions do not, however, correctly describe the deviations from the free ion picture but are just imposed by the exclusion principle.

As just mentioned, the charge-multipole interactions only requires a knowledge of the charge density, so that one has only to substitute a more realistic expression for $\Delta n(\mathbf{r})$ instead of (4′). Assume that we knew the exact number density of electrons. We could then just subtract the density corresponding to a superposition of free ions in order to obtain the true density modification $\Delta n(\mathbf{r})$. This exact $\Delta n(\mathbf{r})$ can be expanded in a set of (e.g. atomic) one-electron function and the expansion can be chosen to be of the form (4′). This implies, as stated in the beginning of this section, that we can consider an expression of the form (1) for discussing the charge-multipole interactions.

The difference from the Heitler–London approach is twofold. (*a*) excited orbitals will appear. This is of no importance, as after making the multipole expansion as was done in [1] and summing over all single particle states we are left with certain functions of the nuclear positions only, and the parameters (derivatives) associated with these functions will not be calculated theoretically but be connected to experimentally known quantities.

(*b*) The dependence on the nuclear position of the expansion coefficients $d_{\mu\nu}$ will be radically different. Instead of the simple dependence given in (2) and (3) the $d_{\mu}{}^{\nu}$ will now depend on the whole configuration of the nuclei.

To continue the discussion, it seems simplest to argue in the language of perturbation theory and start by considering the perturbation of a single free ion at the origin, in the field of the lattice. The contribution to the perturbing potential from an ion not too close to the origin can be represented as that due to a point charge and a sequence of multipoles of higher orders. Representing the contribution from all other ions in that way and summing over the whole lattice, one can finally expand the total perturbing potential around the origin in spherical harmonics and thus separate the polarisation of the ion at the origin into dipolar, and higher multipole contributions. The coefficients in (4′) could in principle be determined by such an approach and will obviously depend on the whole nuclear configuration. The representation of the perturbing potential as that due to a lattice of point charges and multipoles is, however, inadequate for ions close to the origin, partly because of the finite extension of the charge clouds, but still more important because of the exclusion principle (which provides the only deformation mechanism in the Heitler–London scheme). It seems reasonable to divide the coefficients $d_{\mu\nu}$ in (4′) into two parts; one corresponding to the polarisation of the ion due to the field from the charges and multipoles on the lattice and one due to the exclusion principle and the finite extension of the surrounding ions, and we write accordingly

$$d_{\mu\nu} = d'_{\mu\nu} + d''_{\mu\nu}, \tag{5}$$

where $d'_{\mu\nu}$ represents the short-range deformation or exchange deformation and $d''_{\mu\nu}$ corresponds to the ordinary polarisation in a lattice of point charges and multipoles. This division of the coefficients into two parts may seem somewhat arbitrary but can be given a well-defined meaning. Assume that the coefficients $d_{\mu\nu}$ have been found by a complete perturbation treatment. They would then depend explicitly on the charges and multipoles on the lattice. Putting all charges and multipoles equal to zero, we will be left with a remainder which can only be due to exchange and the finiteness of the ions, thus defining the separate contributions $d'_{\mu\nu}$ and $d''_{\mu\nu}$ properly.

The division of $d_{\mu\nu}$ according to (5), divides the last term in (1) into two terms, one due to short-range deformations and one due to electronic polarisation, so that the lattice potential can be written as

$$\Phi = \Phi_{\text{coul}} + \Phi_{\text{rep}} + \Phi_{\text{s.r.def}} + \Phi_{\text{pol}}, \tag{6}$$

where now the two last terms can be discussed separately.

The deformation term in (6), having the same form as the last term in (1) with $d_{\mu\nu}$ replaced by $d'_{\mu\nu}$ according to (5) can now be further reduced if the dependence of the $d'_{\mu\nu}$ on the nuclear position were known. Generally the $d'_{\mu\nu}$ will be complicated functions of the nuclear positions of the ions in the neighbourhood of those associated with μ and ν. However there are reasons to believe (and anyway simplest to assume) that the (exchange) deformation is mainly a pairwise deformation, and that the many-body contribution to $d'_{\mu\nu}$ will be of secondary importance. This assumption is very closely connected to our earlier assumption about the repulsive interaction and the breakdown of either of those two would with almost certainty imply the breakdown of the other. This assumption is completely analogous to the corresponding one by Dick and Overhauser in formulating the shell model. Accordingly we write $d'_{\mu\gamma} = d'_{\mu\nu}(|\mathbf{r}_{G_\mu} - \mathbf{r}_{G_\nu}|)$ and we assume that $d'_{\mu\mu} = \sum_G e'_{\mu\mu}(|\mathbf{r}_G - \mathbf{r}_{G_\mu}|)$, where the $e'_{\mu\mu}$ are chosen such that the integrated deformation charge distribution is zero for each ion pair. Our assumption implies that the form of the contribution to the lattice energy is the same as in the Heitler–London approximation, with the modifications that the $d'_{\mu\nu}$ are no longer simply the overlap integrals and the summation over μ and ν may include other states than those present in a free ion. Accordingly the integrals in $\Phi_{\text{s.r.def.}}$ can be expanded in the same way as described in [1] and after summation over μ and ν one arrives at the formula (4) in [2], if only the first two terms in the expansion are considered. From that point the treatment is given in [1] and [2] and will specifically give the relations between the parameters and elastic constants and effective charge found in (18), in [1] and [21] in [2].

To investigate the polarisation contribution to the lattice potential it seems to be more advantageous to consider the perturbation expression for the energy rather than try to find the coefficients $d''_{\mu\nu}$ by perturbation methods. In this way one can also easily relax our strict subdivision into charge–multipole and multipole–multipole interaction and will have a systematic way of considering all contributions of importance. A complete perturbation treatment for overlapping ion is exceedingly difficult to carry through. We are, however, primarily interested in finding an approximate form for the dependence on the nuclear position only, and the polarisabilities will anyway be taken from experimental data. The dependence on nuclear positions can however be found with good approximation by considering the ions as nonoverlapping.[1] One has then to be careful to correct the expression in such a way that the short-range deformation effects will be accounted for—in lowest order this implies replacing the charge of a free ion by an effective charge.[2] In [2] the dipolar contribution was calculated in a more direct way, by solving directly the field equation giving the force on a given ion due to the polarisation. The result is given in eq. (28), ref. [2]. Straightforward second-order perturbation theory leads to the first term in (28), [2], in an expansion of (28) in powers of the polarisabilities but with the actual ionic charge instead of the effective, which is, of course, due to the neglect of short-range deformation in the perturbation treatment. A tedious analysis of the structure of the higher terms shows that the full expansion, as far as only dipolar polarisation is considered, can be approximately summed to give the result (28), [2], as it must be. As the calculations are very tedious and do not give any further insight, they are not reproduced here.

Both the shell model and our approach take only dipolar polarisation into consideration. The ion–quadrupole coupling is certainly by no means small and should properly be included. This interaction has been discussed by Herpin [14] who derived a formal expression for the difference $c_{12}-c_{44}$, and, using a rough estimate of the quadrupole polarisabilities, he found this contribution to be very important. The difficulty of including such interaction in our scheme is entirely of a practical nature, since the quadrupole polarisabilities are not known either theoretically or experimentally to an acceptable accuracy. Nor is it possible to introduce the quadrupole polarisabilities as parameters from the beginning and determine them through the relations between the parameters of our scheme and the experimentally known quantities, because the number of parameters of our scheme is already somewhat larger than the number of experimental data available.

Discussion

From the discussion in the preceding sections it should be clear that the essential physical content of our approach and that of the shell model is essentially the same. In both schemes two important effects are taken into consideration beyond the Born model: the effect of the short-range deformations, which are largely due to the exclusion principle, and the ordinary dipolar polarisation. In neither of these two approaches are the parameters of the scheme actually computed from any microscopic model but are determined through their relations to experimentally known quantities and are therefore both semi-phenomenological in their nature. In our approach both these effects enter through coefficients in the equations of motion, which have a rather complicated many-body structure. In the shell model the coefficients have a simpler structure, but, instead, the order of the secular equation is doubled, because two displacement vectors have to be considered for each ion in the lattice, one for the displacement of the nucleus from its equilibrium (or mean) position as in ordinary lattice theory and one additional displacement vector describing the motion of the outer spherical shell with respect to the ion core. Evidently the schemes are very closely related although not mathematically the same. For the

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[1] For the general structure of such a perturbation treatment of alkali halides, the reader is referred to an article by Herpin [14], where he considers the elastic properties on the basis of second-order perturbation theory.

[2] This approximation accounts for the coupling between the polarisation and the short range deformation in a crude average sense only and will be reconsidered in a forthcoming publication.

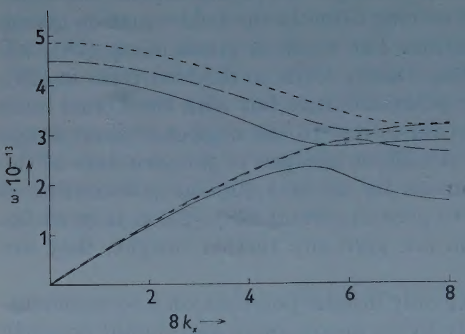

Fig. 1.

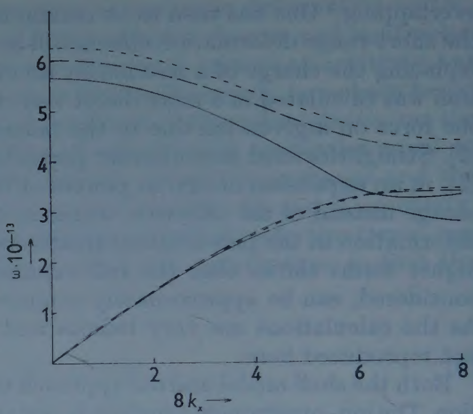

Fig. 2.

Fig. 1. The longitudinal branches of vibration for KCl (*a*) - - -, (*b*) — —, (*c*) ———.

Fig. 2. The longitudinal branches of vibration for NaCl (*a*) - - -, (*b*) — —, (*c*) ———.

somewhat simpler case of Ge it has been proved by Lax[1] that the shell model is mathematically equivalent to the theory developed by him including quadrupole–quadrupole interactions, and which is based on very analogous considerations as ours.

Using a simplified version of the formal treatment given in [2], a preliminary application to KCl and NaCl was made and has been reported in [3]. This calculation was done just to enable a consistent comparison between three approximations: (*a*) the Born model with nearest neighbour repulsive interactions, (*b*) the extended model where the short-range deformation was taken into account in an approximate way and (*c*) the full scheme including both short-range deformations and the dipolar polarisation. The dispersion curves according to (*c*) for longitudinal oscillations in the (100) direction showed an interesting behaviour, having a pronounced dip in the acoustic branch near the zone boundary (Figs. 1 and 2). It was not clear whether this dip was a real physical effect or spuriously introduced through the approximate nature of the theory. Recent neutron diffraction data for NaI [15] give strong support to the iden that the effect is real and probably characteristic of several alkali halides. The shell model has been successfully applied to NaI and the theoretical dispersion curves are in good agreement with the experimental data. Applications of our scheme to NaI as well as several other alkali halides are now under progress.

I wish to thank Professor I. Waller for many interesting discussions about these matters.

Institute of Theoretical Physics, University of Uppsala

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